Graphical abstract

Surface-modified Concentration-gradient Ni-rich Layered Oxide Cathodes for High-energy Lithium-ion Batteries

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Abstract

Concentration-gradient layered $\text{Li}[\text{Ni}_{0.8}\text{Co}_{0.2}]_{0.7}[\text{Ni}_{0.2}\text{Mn}_{0.8}]_{0.3}\text{O}_2$ oxide with Ni-rich in the core and Mn-rich in the surface region has been synthesized through a condition-controlled tank reactor reaction. While the Ni-rich core facilitates high capacity, the Mn-rich surface enables good cyclability and thermal stability. The concentration-gradient sample exhibits a higher capacity of 204 mA h g^{-1} at C/5 rate with superior cyclability and thermal stability compared to the constant-concentration $\text{LiNi}_{0.62}\text{Co}_{0.14}\text{Mn}_{0.24}\text{O}_2$ sample, which has the same net Ni, Co, and Mn contents as those present in the concentration-gradient sample. The concentration-gradient sample was also coated with a thin layer of Al_2O_3 on the surface to stabilize the electrode/electrolyte interface and thereby further improve the electrochemical performance. Both the structural (gradient structure) and surface (Al_2O_3 coating) modifications help suppress side reactions between electrode and electrolyte and reduce the decline in voltage during cycling. The Al_2O_3 -coated concentration-gradient sample exhibits improved long-term cyclability, rate capability, and thermal stability compared to the pristine uncoated sample.

Keywords: Lithium-ion batteries; cathodes; layered oxides; nickel-rich oxides; concentration-gradient oxide; surface coating

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1. Introduction

The ever increasing demand for portable telecommunication devices, laptops, and hybrid vehicles has given rise to the increased production of high-energy-density lithium-ion batteries (LIBs). Since the development of the first LIB by Sony in 1991, extensive research has been carried out over the 14 years to replace the layered LiCoO_2 cathode because of its limitations that include high cost, low capacity, toxicity, and chemical instability at high potentials [1-7]. In the past, LiNiO_2 has been considered as an attractive cathode material due to its higher discharge capacity and lower cost. However, LiNiO_2 also has several disadvantages, such as difficulties to keep all nickel as Ni^{3+} and obtain a well-ordered material, poor cycling performance, and unsatisfactory thermal stability [8-11]. To overcome these difficulties, much effort has been focused on composition modifications, synthesis condition optimization, and surface modifications to improve the performance of LiNiO_2 . For example, the partial substitutions of Co, Mn, or other ions for Ni is one of the approaches that has been pursued to lower the cost and improve the reversible capacity and structural stability during cycling [5,12-14].

Particularly, the composition $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ has attracted much attention as 4 V cathode materials in the past years [15-17]. However, the $\text{Li}_{1-x}\text{Ni}_{0.8}\text{Co}_{0.2}\text{O}_2$ electrodes are structurally unstable during thermal runaway reactions due to oxygen release from the host structure. In addition, the released oxygen and the strong oxidizing power of Ni^{4+} ions can cause slow decomposition of the liquid organic electrolyte and lead to safety problems [15, 18-20]. These issues make it difficult for conventional Ni-rich cathode materials to be adopted in practical cells for large-scale applications such as electric vehicles. Recently, Sun's group reported Ni-rich concentration-gradient cathode materials, where the concentration of Ni decreases and Mn increases gradually from the centre towards the surface to improve the cycle life and safety compared to the constant-concentration nickel-rich oxides [21-23]. These materials have shown

superior performance and are promising. Further improvements could be made by coating the surface of such cathodes with an inert material to form an artificial protective layer that serves as a substitute for the solid electrolyte interphase (SEI) and **also** stabilizes the electrode/electrolyte interface [24-26]. As one of the excellent coating materials, Al_2O_3 has been employed to coat the surface of both the anode and cathode materials for LIBs [27-30].

We present here the synthesis, characterization, and electrochemical evaluation of the concentration-gradient $\text{Li}[\text{Ni}_{0.8}\text{Co}_{0.2}]_{0.7}[\text{Ni}_{0.2}\text{Mn}_{0.8}]_{0.3}\text{O}_2$ cathodes in which the $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ core and $\text{LiNi}_{0.2}\text{Mn}_{0.8}\text{O}_2$ surface could facilitate, respectively, high capacity and cycle stability. The concentration-gradient sample is then coated with Al_2O_3 via a chemical process to further improve the electrochemical performance. The performances of the concentration-gradient sample before and after coating with Al_2O_3 are compared with those of a constant-concentration sample that has the same net Ni, Co, and Mn contents as in the concentration-gradient sample.

2. Experimental

2.1 Materials Synthesis

The constant-concentration $[\text{Ni}_{0.8}\text{Co}_{0.2}](\text{OH})_x$ and $[\text{Ni}_{0.62}\text{Co}_{0.14}\text{Mn}_{0.24}](\text{OH})_x$ were synthesized by a one-step co-precipitation process. The appropriate amounts of $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$, $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$, and $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ dissolved in deionized water were used as the starting solutions for $[\text{Ni}_{0.8}\text{Co}_{0.2}](\text{OH})_x$ (cationic ratio of Ni : Co = 8 : 2) and $[\text{Ni}_{0.62}\text{Co}_{0.14}\text{Mn}_{0.24}](\text{OH})_x$ (cationic ratio of Ni : Co : Mn = 0.62 : 0.14 : 0.24), respectively. The solution was then pumped continuously into a stirred tank reactor under nitrogen atmosphere. At the same time, 2.0 M aqueous NaOH and desired amount of ammonium hydroxide solution were pumped into the reactor. The mole ratio of metal ions to ammonia was 2 : 1, and the pH was controlled to be at 11 with aqueous NaOH. The concentration of

the solution, pH, temperature, and stirring speed of the solution in the tank reactor were carefully controlled for reproducibility. The concentrations of metal ions and ammonia solutions were 2 mol L⁻¹ and 0.5 mol L⁻¹, respectively. For the concentration-gradient [Ni_{0.8}Co_{0.2}]_{0.7}[Ni_{0.2}Mn_{0.8}]_{0.3}(OH)_x synthesis, the resulting [Ni_{0.8}Co_{0.2}](OH)_x was continuously reacted with a solution containing required amounts of NiSO₄·6H₂O and MnSO₄·H₂O (cationic ratio of Ni : Mn = 2 : 8). The co-precipitated precursor powders of [Ni_{0.8}Co_{0.2}](OH)_x, [Ni_{0.62}Co_{0.14}Mn_{0.24}](OH)_x and [Ni_{0.8}Co_{0.2}]_{0.7}[Ni_{0.2}Mn_{0.8}]_{0.3}(OH)_x were filtered, washed with deionized water, and dried at 100 °C over night. Finally, these metal hydroxide precursors were thoroughly mixed with 3% excess LiOH·H₂O (Li : M = 1.03 : 1) to compensate for any volatilization of Li during synthesis and heated at 800 °C for 15 h in air.

To produce the Al₂O₃ coating on the concentration-gradient sample, 0.06 g of aluminium isopropoxide was dissolved in 20 mL of ethanol and stirred at 50 °C for half an hour. Then 2 g of the prepared concentration-gradient oxide powder was slowly added and thoroughly mixed for another hour. The obtained mixture was dried at 110 °C overnight and then heated at 400 °C for 5h.

2.2 Materials Characterization

The phase-purity and crystal structure of the obtained materials were studied with X-ray diffraction (XRD, Phillip) with Cu K α radiation from 10 to 80° at a scan rate of 0.03° s⁻¹. Field emission scanning electron microscopy (FE-SEM, Quanta 650), scanning transmission electron microscopy (STEM, S-5500), and transmission electron microscopy (TEM, JEOL 2010F) were used to examine the morphologies, crystalline structures, and elemental distributions of the samples. The total average chemical compositions in the

synthesized samples were analyzed with a Varian 715-ES inductively coupled plasma-atomic emission spectrometer (ICP-AES).

2.3 Electrochemical Evaluation

The electrochemical characterizations were performed with 2032-type coin cells assembled in an Ar-filled glove box with the synthesized cathode materials, Li metal anode, 1M LiPF₆ in ethylene carbonate (EC)/dimethyl carbonate (DMC) (1/1 by volume) electrolyte, and polypropylene separators. The cathode was fabricated with a mixture consisting of the synthesized layered oxide powder (80 wt.%), carbon black (10 wt.%), and polyvinylidene fluoride (PVDF) (10 wt.%) in N-methyl-2-pyrrolidone (NMP). The slurry was spread onto an aluminum foil and dried in a vacuum oven at 110 °C. The discharge-charge cycling was performed between 4.5 and 2.7 V (*vs.* Li/Li⁺) at room temperature at different C-rates of C/5 to 5C with an Arbin Instruments cycler (1C = 180 mA g⁻¹). Cyclic voltammetry (CV) testing was performed between 4.5 and 2.7 V (*vs.* Li/Li⁺) with a scan rate of 0.1 mV s⁻¹ (VoltaLab PGZ 402, Radiometer Analytical).

2.4 Thermal properties

The thermal stability of the samples was analyzed with differential scanning calorimeter (DSC). For the DSC experiments, the assembled cells were charged to 4.3 V and disassembled in an Ar-filled glove box, followed by removing the wet cathode and sealing it into a stainless steel crucible with a perforated lid and a gold foil seal. The DSC data were then collected with a Netzsch STA 449 thermal analysis system at a heating rate of 10 °C min⁻¹ up to 400 °C and nitrogen purge gas.

3. Results and discussion

The XRD patterns of the synthesized concentration-gradient $\text{Li}[\text{Ni}_{0.8}\text{Co}_{0.2}]_{0.7}[\text{Ni}_{0.2}\text{Mn}_{0.8}]_{0.3}\text{O}_2$ (hereafter designated as CG) and the constant-concentration $\text{LiNi}_{0.62}\text{Co}_{0.14}\text{Mn}_{0.24}\text{O}_2$ (hereafter designated as CC) samples are presented in Fig. 1, and the patterns of the corresponding hydroxide precursors are given in Fig. S1. All of the observed peaks of the synthesized oxides in Fig. 1 could be indexed on the basis of the hexagonal $\alpha\text{-NaFeO}_2$ structure with $R\text{-}3m$ space group as seen in Fig. 1. Although the CG sample was synthesized by a two-step synthesis with two different hydroxide compositions at the interior and exterior, cationic diffusion could occur during the high-temperature firing, so we presume a smooth variation in cationic compositions from the interior to the exterior without any abrupt changes at the interface between the two compositions. The Al_2O_3 -coated CG sample (hereafter designated as CG- Al_2O_3) also displays a pattern similar to the uncoated samples without any extra peaks due to the smaller amount and/or the poor crystallinity of Al_2O_3 . Both the coated and uncoated CG samples show similar lattice parameters of, respectively, $a = 2.875$ and $c = 14.234$ and $a = 2.874$ and $c = 14.230$, indicating that the Al_2O_3 -coating did not cause any significant changes in the layered oxide.

The SEM images of the samples shown in Fig. 2 and Fig. S2 indicate spherical morphology and the maintenance of the particle size of the hydroxides after the high-temperature treatment with lithium hydroxide. Fig. 2b and 2d show the energy dispersive spectroscopic (EDS) line scan results of, respectively, the CC and CG particles. The relative elemental Mn/Ni intensity ratio across the CG sample particle increases from the center to the surface, while that of the CC sample particle almost remains constant from the center to the surface. This indicates the formation of a Mn-rich phase along the surface and Ni-rich phase along the center in the CG sample. The Al_2O_3 -coating layer can hardly be seen in the SEM image shown in Fig. 2e due to

the rather small thickness. However, the existence of Al_2O_3 in the coated sample can be evidenced by the EDS data illustrated in Fig. 2f. The carbon content seen is due to the carbon tape used during SEM characterization.

Fig. 3 shows the TEM and high-resolution TEM (HRTEM) images of the three synthesized samples. Both the CC and CG samples in Fig. 3a and 3b display a bare and clean surface and an apparent layered structure with an interplanar spacing of *ca.* 0.47 nm corresponding to the (003) plane. In order to determine the thickness of the Al_2O_3 layer, the Al_2O_3 -coated CG particle was observed by TEM as well. The TEM micrograph in Fig. 3c shows that the size and morphology of the layered oxide particles are maintained during the Al_2O_3 coating process. The high magnification TEM image of the outer edge of the particle (Fig. 3d) indicates an Al_2O_3 coating thickness of around 10 nm.

The electrochemical performances of the as-prepared CC, CG, and CG- Al_2O_3 cathodes were evaluated in half cells with a metallic lithium anode. Fig. 4a-c show the cyclic voltammogram (CV) plots of the first five cycles for all the three electrodes at a sweep rate of 0.1 mV s^{-1} within a potential window of 2.7 to 4.5 V (vs. Li/Li^+). As can be seen, all the three samples undergo similar Li^+ -ion extraction/insertion. The initial anodic peaks at about 4.2 V corresponded to the oxidation process of $\text{Ni}^{2+}/\text{Co}^{3+}$ to higher oxidation states. The potential differences among the redox peaks of CC, CG, and CG- Al_2O_3 at the fifth cycle are, respectively, 188, 157, and 150 mV, indicating a slightly reduced polarization of the electrode from CC to CG to CG- Al_2O_3 samples [31,32]. These CV results are consistent with the increasing electrochemical performances of the samples from CC to CG to CG- Al_2O_3 shown below.

To investigate the structural stability of the cathodes, charge-discharge profiles at C/5 rate at different stages of cycling, *i.e.*, 1st, 2nd, 10th, 20th, and 50th cycles, are shown in Fig. 5a-c and Fig. S3. The polarization loss and decline in voltage during cycling decreases from the CC sample to the CG sample, and then to the CG-Al₂O₃ sample. In the CG sample, the high Mn content (or low Ni content) on the surface compared to that in the CC sample, suppresses the side reactions with the electrolyte and thereby decreases the insulating SEI layer formation and voltage decline during cycling. In the CG-Al₂O₃ sample, the Al₂O₃ coating suppresses the side reactions further and thereby decreases the voltage decline further. Thus, the data demonstrate that the structural and surface modifications suppress side reactions of the cathode surface with the electrolyte and thereby improve lithium diffusion through the surface and enhance the electrochemical performance.

Fig. 6a shows the discharge capacity retention at C/5 of the CC, CG, and CG-Al₂O₃ samples. Although the CC sample retains only 62.6% of its initial discharge capacity value after 100 cycles (fading from 206 mA h g⁻¹ to 129 mA h g⁻¹), the CG sample shows much higher capacity retention of around 80% (fading from 204 mA h g⁻¹ to 163 mA h g⁻¹). The rapid capacity fade of the CC sample is due to the direct exposure of a high content of nickel ions on the surface to the electrolyte at high potentials and the consequent chemical decomposition of both the surface of the electrode and the electrolyte. In the case of CG-Al₂O₃ sample, the first discharge capacity value of 195 mA h g⁻¹ increases slightly in the beginning four cycles, which could be ascribed to the improvement in lithium-ion diffusion through the Al₂O₃ coating as the electrode is cycled. More importantly, after being activated during the first several cycles, the discharge capacity remains much more stable than the other two uncoated electrodes. The

discharge capacity decreases from 197 mA h g⁻¹ in the 4th cycle to 175 mA h g⁻¹ in the 100th cycle.

To further assess the cyclability of the CG-Al₂O₃ electrode, an aggressive test profile was selected where the cells were charged up to 4.5 V and cycled at 55 °C (Fig. 6b). All three electrodes show a high initial discharge capacity of over 205 mA h g⁻¹. However, the CC electrode retains only 51% of its initial capacity after 50 cycles, while the CG and CG-Al₂O₃ samples retain, respectively, 81% and 89% under the same cycling conditions. The high capacity retention of the CG-Al₂O₃ electrode at high temperatures demonstrates the criticality of the cathode surface in contact with the electrolyte with Ni-rich cathodes to obtain high performance.

Fig. 7a compares the rate capability of the CC, CG, and CG-Al₂O₃ samples from C/5 to 5C and then back to C/5 rate. Clearly, the rate capability increases from the CC to CG, and to CG-Al₂O₃ sample. The superior rate capability of CG and CG-Al₂O₃ electrodes were further analyzed by electrochemical impedance spectroscopy (EIS). The Nyquist plots of the CG and CG-Al₂O₃ electrodes after the 10th cycle shown in Fig. 7b exhibit a semicircle at the high-medium frequency region and an inclined line at the low frequency region, which correspond, respectively, to interfacial resistance and Li⁺-ion diffusion resistance inside the cathode particle. The impedance spectra were fitted with the equivalent circuit, shown as an inset in Fig. 7b, where R_s represents the bulk electrolyte ionic resistance, and R_i is associated with the interfacial resistance between the active material and electrolyte, which includes the charge-transfer resistance (R_{ct}) and any passivation surface film resistance (R_p). The W (Warburg impedance) as reflected by the declined line at low frequency corresponds to the Li⁺ ion diffusion resistance in the bulk phase of the active material. The fitted result reveals the R_s values to be 8.6 and 6.1 ohm for the CG sample and CG-Al₂O₃ sample, while the R_i values are 75.5 and 51.3 ohm for CG sample and the

CG-Al₂O₃ sample, respectively. This result suggests that the CG-Al₂O₃ electrode has relatively lower kinetic barrier for Li⁺-ion insertion/extraction, thus enabling a fast faradic reaction and the enhanced high-rate performance of the CG-Al₂O₃ electrode compared to the uncoated electrode (Fig.7a). The uncoated CG electrode shows higher electrolyte resistance and interfacial resistance, which can be attributed to the consumption of electrolyte and deposition of thick SEI film on the cathode surface during the charge-discharge process, leading to its fast capacity degradation and poor rate capability.

The thermal stability and safety of cathode materials are critical in considering them for practical cells. Accordingly, a differential scanning calorimetry (DSC) study was performed on all three cathodes after charging the cells to 4.3 V in the presence of 1M LiPF₆/EC-DMC electrolyte. As shown in Fig. 8, no heat flow was detected with DSC within the temperature range from 100 °C to 150 °C for all three samples. For the CC electrode, the onset temperature of the exothermic reaction occurred at around 278°C, with a peak at 286 °C. The CG electrode, on the other hand, shows a higher onset temperature (283°C) and slightly reduced heat generation compared to the CC electrode, which could be due to the high Mn content in surface. The onset temperature of 283 °C is very close to the temperatures reported for the concentration-gradient samples Li[Ni_{0.64}Co_{0.18}Mn_{0.18}]₂O₂ (270 °C) and Li[Ni_{0.72}Co_{0.18}Mn_{0.10}]₂O₂ (280 °C) [21, 34]. The slightly higher temperature of 283 °C for our sample may be ascribed to the lower Ni content of 0.62 and higher Mn content of 0.24. For a comparison, as shown in Fig. S4, the lower onset temperature of the Mn-free and high-nickel content LiNi_{0.8}Co_{0.2}O₂ electrode indicates a very unstable cathode material because of the easier oxygen release from the host structure [33]. Interestingly, the CG-Al₂O₃ electrode shows the highest onset temperature and peak temperatures

of, respectively, 295 °C and 301 °C. Also, the CG-Al₂O₃ electrode shows the lowest heat generation, which is consistent with the previous findings with other Al₂O₃ coated sample [35].

4. Conclusions

A concentration-gradient cathode with a Ni-rich interior and a Mn-rich surface has been synthesized and evaluated as a cathode in lithium-ion cells. It exhibits a high reversible capacity of 204 mA h g⁻¹ with good cycling and thermal properties due to the suppressed surface reaction with the electrolyte. Furthermore, surface-coating of the concentration-gradient sample with Al₂O₃ provides further improvement in cycle life, rate capability, and thermal stability. The Al₂O₃-coated sample retained ~ 89% of the capacity after 100 cycles at a C/5 rate. The results demonstrate the importance of having optimum surface compositions and structures to enhance the commercial viability of the Ni-rich layered oxide cathodes for the next-generation of lithium-ion batteries.

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Figure Captions

Fig. 1(a) XRD patterns of CC, CG, and CG-Al₂O₃ samples and (b) Rietvelt refinement results of the XRD data of the CG-Al₂O₃ sample.

Fig. 2 SEM images of the (a) CC, (c) CG, and (e) CG-Al₂O₃ samples. (b) EDS line-scanning profile of Mn content relative to the Ni content in the CC particle. (d) EDS line-scanning profile of the Mn content relative to the Ni content in the CG particle. (f) EDS spectra of the Al₂O₃-coated CG particle.

Fig. 3 TEM and HRTEM images of (a) CC, (b) CG, and (c,d) CG-Al₂O₃ samples.

Fig. 4 First five CV cycle curves of the (a) CC, (b) CG, and (c) CG-Al₂O₃ electrodes at a scan rate of 0.1 mV s⁻¹ between 2.7 and 4.5 V.

Fig. 5 Charge-discharge curves between 2.7 and 4.5 V of the (a) CC, (b) CG, and (c) CG-Al₂O₃ electrodes at room temperature.

Fig. 6 Comparison of the cycling performances (C/5) of the three cathodes(a) at room temperature and (b) at 55 °C.

Fig. 7 (a) Rate performances at various current densities from C/5 to 5C (1C = 180 mA g⁻¹) of the CC, CG, and CG-Al₂O₃ electrodes and (b) electrochemical impedance spectra (Nyquist plots) of the CC, CG, and CG-Al₂O₃ electrodes at the fully charged states after 10 charge-discharge cycles.

Fig. 8 Differential scanning calorimetry traces showing the heat flow from the reaction of the electrolyte with the CC, CG, and CG-Al₂O₃ electrodes charged to 4.3 V.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8